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Deactivation in continuous deoxygenation of C_{18}-fatty feedstock over Pd/C

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A promising type of biofuel is the so-called "renewable diesel", ie. alkanes produced via deoxygenation of fats and oils. The most selective heterogeneous catalysts for decarbonylation and decarboxylation (loss of fatty acid functionality as CO or CO_2) are supported nanoparticles of platinum and palladium.
It is important to understand mechanistic details and deactivation behavior in the deoxygenation reactions to optimize catalyst performance, especially when working with more complex and often troublesome feedstocks like abattoir waste or grease from cooking. To this date only a few profound studies have been published about the deoxygenation of fatty feedstocks, but these have mostly dealt with free fatty acids. Studies until now indicate a somewhat complex reaction network between gas and liquid phases during deoxygenation.

Recently, a remarkable time-dependent shift in the gas production from CO_2 to CO has been observed during deoxygenation by several authors [1,2]. It has also been found that deactivation takes place via occlusion of the pores of the catalyst support [1,3], connected with the presence of unsaturated compounds leading to coking [4].

In this work, continuous deoxygenation has been performed of respectively neat stearic acid, ethyl stearate and tristearin at 300°C in a packed-bed reactor over an egg-shell impregnated catalyst of 2 wt% Pd on Sibunit carbon beads. 5% H_2/Ar at 20 bar was employed as sweeping gas, but after 75 h time-on-stream (stearic acid: 96 h) of uniform operation the gas atmosphere was changed to pure Ar. Both liquid and gas samples were collected for offline GC analysis during each experiment, and CO and CO_2 were measured by online IR.

The alkane production was in the order of reactants: stearic acid > ethyl stearate > tristearin, both initially and after 75 h (see Table 1). However, the switch to pure Ar gas led to swift deactivation, especially for the tristearin. The stearic acid furnished some hydrocarbons after the change to pure Ar sweeping gas, especially unsaturated C_{17}-compounds, while the ester feedstocks did not convert to hydrocarbons without H_2 in the feed.

Table 1: 300°C, 20 bar 5% H_2/Ar gas, 2 wt% Pd/Sibunit

	Deoxygenation to alkanes, yield			Post-reaction catalyst pore vol.
	After 0 h Gas: 5% H_2/Ar	After 75 h Gas: 5% H_2/Ar	After 150 h Gas: Ar	(Fresh cat.: 361 m^2/g)
Stearic acid	>90%	75%	3%	193 m^2/g
Ethyl stearate	>90%	62%	0%	229 m^2/g
Tristearin	85%	28%	0%	200 m^2/g

After each reaction the catalyst beads were sampled in 5 batches and subjected to BET analyzes. No monotonic deactivation profile in axial direction was observed in the reactor although this has previously been observed [1]. The ethyl stearate catalyst appears to be least deactivated with respect to surface area loss (Table 1).

An experiment switching between neat dodecane and stearic acid was conducted over neat Sibunit beads in Ar gas, affording 5% conversion of stearic acid and revealing a startup-time of 3-4 h to reach steady-state. It can thus be concluded that the palladium-containing catalyst was completely deactivated after exposure to stearic acid for the entire 150 h experimentation.

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